

Chiral Stable Phenalenyl Radical: Synthesis, Electronic-Spin Structure, and Optical Properties of [4]Helicene-Structured Diazaphenalenyl**

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Helicenes are *ortho*-annulated polycyclic aromatic molecules with nonplanar helical conjugation of the π -electron system.^[1] These aromatic molecules have attracted special attention not only because of the nonplanarity of the π -conjugated skeleton but also because of their inherent helical chirality. Recent developments in helicene chemistry have focused on the synthesis and optical resolution of new helicene derivatives^[2] as well as on asymmetric catalysts,^[3] molecular recognition,^[4] and chiroptical functionalities.^[5,6] However, almost all of the helicene derivatives investigated so far are intrinsically closed-shell electronic systems except for a few examples.^[7] Thus, the chemistry of open-shell helicenes has been little explored in the past; to our knowledge there have been no experimental studies on helicene-based nonplanar chiral neutral π -radical systems.^[8]

As stable open-shell molecular systems possessing chirality, a number of nitroxide-based chiral neutral radical derivatives have been synthesized and characterized.^[9] These systems were constructed by introducing a substituent having one or more asymmetric carbon atoms to an achiral nitroxide radical skeleton based on, for example, pyrrolidine-1-oxyl and α -nitronylnitroxide. By taking advantage of the localized unpaired electronic spin on the N–O moiety, chiral molecular magnets and paramagnetic organic chiral liquid crystals have extensively been implemented.^[9b,10]

In contrast to the nitroxide radicals, in phenalenyl (PLY in Figure 1), a planar neutral hydrocarbon π -radical, the electronic spin is extensively delocalized over the whole molec-

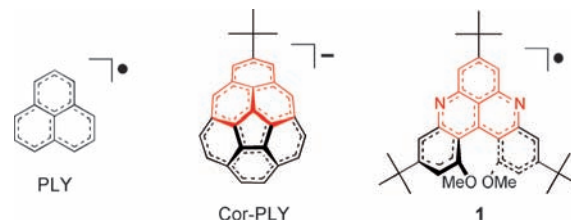


Figure 1. Chemical structures of PLY, Cor-PLY, and **1** (the *P* enantiomer is arbitrarily chosen).

ular skeleton.^[11] As a consequence, phenalenyl derivatives exhibit unique physical properties and functionalities different from the those of spin-localized neutral radicals such as nitroxide derivatives.^[11,12] Furthermore, our recent study revealed that the highly delocalized electronic structure inherent in phenalenyl also appears in a curved phenalenyl system with a corannulene substructure (Cor-PLY, Figure 1).^[13,14] Cor-PLY is the first nonplanar phenalenyl derivative in the half-century-old phenalenyl chemistry.

These studies have inspired us to design nonplanar π -conjugated chiral phenalenyl radicals based on helicene.^[11b] The chiral neutral π -radical is intriguing not only because of the spin delocalization in the three-dimensional (3D) helical π -conjugated network but also because of optical magnetic properties attributable to the combination of helicene chirality and delocalized electronic spin. Here we report the synthesis, electronic-spin structure, and optical properties of chiral diazaphenalenyl **1** (Figure 1),^[15] in which a benzene ring is fused to a nitrogen-containing [4]helicene-type structure. Thanks to two terminal methoxy groups and three *tert*-butyl groups, radical **1** exhibits high configurational and chemical stability, enabling us to experimentally characterize both chiral and racemic species of **1** with the help of theoretical calculations. Solution-phase ESR and ENDOR/TRIPLE studies indicate that the unpaired electron spin is extensively delocalized over the nonplanar helicenic π -conjugated skeleton. Furthermore, the racemization behavior of **1** was also successfully studied by time-dependent solution-phase circular dichroism (CD) measurements at several temperatures.

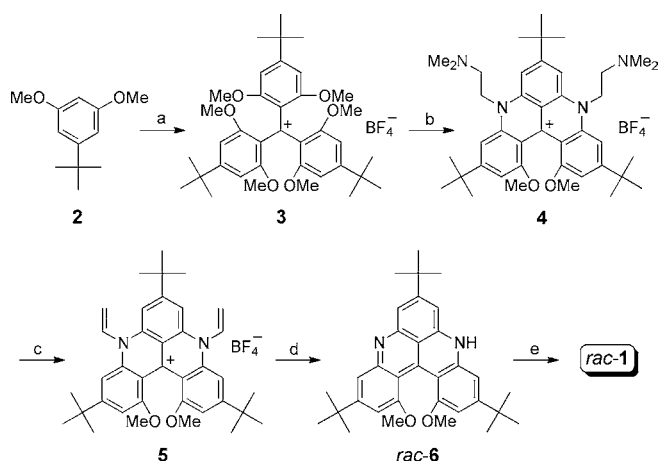
We first prepared the helicenic neutral π -radical **1** as a racemic compound, *rac*-**1**, to evaluate its chemical stability and electronic-spin structure. The five-step synthesis from 1-*tert*-butyl-3,5-dimethoxybenzene (**2**)^[16] is depicted in Scheme 1. Triarylmethyl cation salt **3** was obtained by nucleophilic reaction of lithiated **2** with diethyl carbonate followed by treatment with aqueous tetrafluoroboric acid. A double condensation reaction of **3** with *N,N*-dimethylethylenediamine gave the [4]helicene-type compound **4** in racemic

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Scheme 1. Synthesis of *rac-1*: a) 1. *n*BuLi, Et₂O, reflux, 2. (EtO)₂CO, Et₂O, reflux, 3. aq HBF₄, Et₂O, room temperature, 85%; b) *N,N*-dimethylethylenediamine, *N*-methylpyrrolidone, 110°C, 60%; c) 1. MeI, MeOH, 110°C, 2. *t*BuOK, DMF, room temperature, 3. aq HBF₄ aq, room temperature, 100%; d) 1. aq HBF₄, MeOH, 70°C, 2. aq Na₂CO₃, CH₂Cl₂, room temperature, 94%; e) PbO₂, benzene, room temperature, 99%.

form.^[17] Hofmann elimination reaction of **4** through *N*-methylation with an excess amount of methyl iodide provided the bis(enamine) derivative **5**. The racemic radical precursor *rac-6* was obtained as purple crystals by the removal of the ene groups of **5** under acidic conditions followed by neutralization and recrystallization.^[18] Finally, treatment of *rac-6* with an excess amount of PbO₂ quantitatively gave the desired neutral radical *rac-1* as a red powder. The radical *rac-1* survives in the solid state in air at −30°C for a few weeks and is also extremely stable in degassed solution at room temperature.^[19]

The spin-delocalized nature of the helicenic π -conjugated system was evaluated by liquid-phase ESR and ¹H- and ¹⁴N-ENDOR/TRIPLE measurements of *rac-1* (Figure 2). The ESR spectrum of a solution of *rac-1* (1.0 × 10^{−3} M) in degassed toluene shows a well-resolved hyperfine structure (*g* = 2.0032) (Figure 2a). Hyperfine coupling constants (hfccs) ascribable to the hydrogen and nitrogen nuclei and their relative signs were unequivocally determined by ¹H- and ¹⁴N-ENDOR/TRIPLE spectroscopy (Figure 2c,d). These hfccs were successfully assigned with the help of density functional theory (DFT) calculations (Table 1).^[20] The observed and calculated values are in good agreement. Furthermore, an ESR spectral simulation based on the hfccs obtained by the ENDOR measurements well reproduced the observed spectrum (Figure 2b). Therefore, as illustrated by the calculated spin density distribution (Figure 3), the unpaired electron spin of *rac-1* in solution is extensively delocalized over the whole helicenic π -conjugated system. Importantly, there are large amounts of positive spin density on the 5-, 6-, 8-, 9-, 14-, and 16-positions, demonstrating that a phenalenyl-like topology in spin delocalization is maintained in this nonplanar helicenic π -radical system. In addition, the extended π -conjugated structure of **1** obtained by the fusion of two benzene rings to the diazaphenalenyl skeleton leads to a smaller energy gap between the singly occupied molecular orbital (SOMO) and

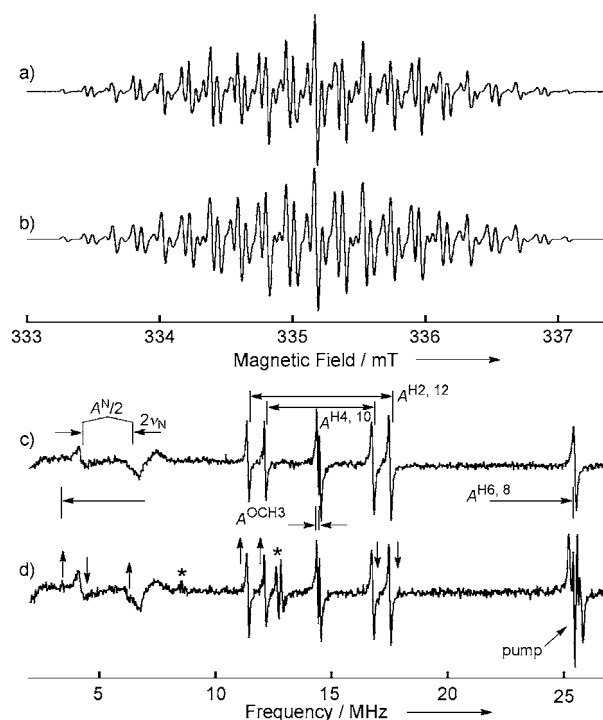


Figure 2. a) Observed ESR spectrum of *rac-1* (1.0 × 10^{−3} M) in degassed toluene at 290 K. The microwave frequency used is 9.39723 GHz and the observed *g*-value is 2.0032. b) The simulated ESR spectrum. c) Observed ¹H- and ¹⁴N-ENDOR and d) ¹H- and ¹⁴N-TRIPLE spectra (pump frequency 25.48 MHz) of *rac-1* (1.0 × 10^{−3} M) in degassed toluene at 290 K. Asterisks denote spurious noise arising from strong RF irradiation. A bump/valley around 7 MHz (c and d) is a ghost signal intrinsic to the double-resonance spectrometer.

Table 1: Observed and calculated hfccs (in units of mT) of *rac-1*.^[a]

	H6, 8	H4, 10	H2, 12	OCH ₃	<i>t</i> Bu	N
Obs ^[b]	−0.785	−0.166	−0.218	±0.004	− ^[d]	+0.369
Calc ^[c]	−0.874	−0.223	−0.264	−0.011	+0.004, ^[e] +0.0003 ^[f]	+0.405

[a] Atom numbering is given in Figure 3. [b] Values and relative signs were determined by ¹H- and ¹⁴N-ENDOR/TRIPLE spectroscopy. [c] Hfcs of the optimized structure calculated at the UB3LYP/6-31G(d,p) level of theory. Considering the molecular symmetry, hfccs for the equivalent nuclei were averaged. [d] Hfcs of *t*Bu protons could not be experimentally determined. [e] *t*Bu protons at the 7 position. [f] *t*Bu protons at the 3 and 11 positions.

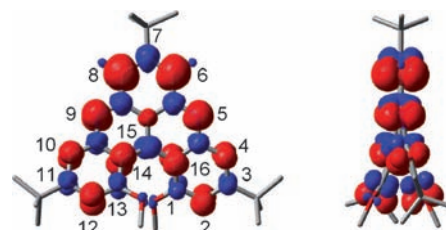


Figure 3. Spin density distribution of **1** (left: top view, right: side view) calculated at the UB3LYP/6-31G(d,p) level of theory ((*P*)-**1** is arbitrarily chosen). Red and blue colors denote positive and negative spin densities, respectively.

the lowest unoccupied molecular orbital (LUMO) than in the parent diazaphenelenyl system (see the Supporting Information).

We chose the oxidation reaction of the chiral phenalene derivatives (*P*)-**6** and (*M*)-**6** as the most reliable method to obtain the chiral radicals (*P*)-**1** and (*M*)-**1** in chemically and enantiomerically pure form. Thus we resolved the racemic phenalene *rac*-**6** by HPLC using a chiral stationary phase.^[21] In analytical HPLC, two fractions with equivalent peak area intensity eluted at around 3.97 min and 7.27 min (see the Supporting Information). The two fractions, which were collected separately by preparative HPLC on a chiral stationary phase, gave typical mirror-image solution-phase CD spectra (see the Supporting Information). These results clearly demonstrate that the two HPLC peaks correspond to the two enantiomers of the chiral phenalene **6**.^[22] The absolute configurations of the first and second fractions were determined as *P* and *M*, respectively, by comparison of the experimental CD spectra with the theoretical ones obtained by time-dependent DFT calculations (see the Supporting Information). Notably, the CD spectra of the chiral phenalenes (*P*)-**6** and (*M*)-**6** in solution at room temperature are almost unchanged after a few days. Time-dependent CD measurements of (*M*)-**6** in *o*-xylene solution at several temperatures (see the Supporting Information) disclosed that the activation energy $\Delta G^\ddagger$ for racemization for **6** (118.8 kJ mol⁻¹) at 303 K is intermediate between the corresponding values for [5]helicene (101.0 kJ mol⁻¹)^[23] and [6]helicene (149.9 kJ mol⁻¹).^[24] The configurational stability of **6** is quite high for a [4]helicene derivative and apparently a result of the steric hindrance of the two terminal methoxy groups.^[25]

Oxidation of the chiral phenalenes (*P*)-**6** and (*M*)-**6** with an excess amount of PbO₂ quantitatively gave the corresponding chiral neutral radicals (*P*)-**1** and (*M*)-**1**, respectively, as red solids. Each chiral radical in degassed toluene solution exhibits a well-resolved hyperfine ESR spectrum identical to that of *rac*-**1** (see the Supporting Information). Similar to *rac*-**1**, these radicals have a high chemical stability: The radicals survive in the solid state in air or in degassed solution for a few weeks.

The optical properties of the chiral neutral π -radicals were investigated by solution-phase CD spectroscopy (Figure 4). A solution of the *P* enantiomer (*P*)-**1** (1.0×10^{-4} M) in toluene shows positive Cotton effects at 308 nm and 460 nm and negative ones at 362 nm and 547 nm (Figure 4a). Notably, the overall molar circular dichroism ($\Delta\epsilon$) of (*P*)-**1** is significantly greater (by one or two orders of magnitude) than that of the α -nitronylnitroxide-based chiral neutral radicals bearing one or more asymmetric carbon atoms.^[26] The larger $\Delta\epsilon$ values of (*P*)-**1** are attributable to the chirality of the helicene unit. The CD spectrum of (*M*)-**1** is a complete mirror image to that of (*P*)-**1**, demonstrating that they are enantiomers. Similar to the case of the chiral phenalenes **6**, their CD spectra were almost unchanged after a few days at room temperature. Therefore, in order to quantitatively evaluate their thermal racemization behavior, we examined time-dependent decay profiles of the CD intensity of (*P*)-**1** at 315 nm in a degassed *o*-xylene solution at 313 K, 323 K, and 333 K (Figure 4b). The racemization behavior follows first-order kinetics, and thus

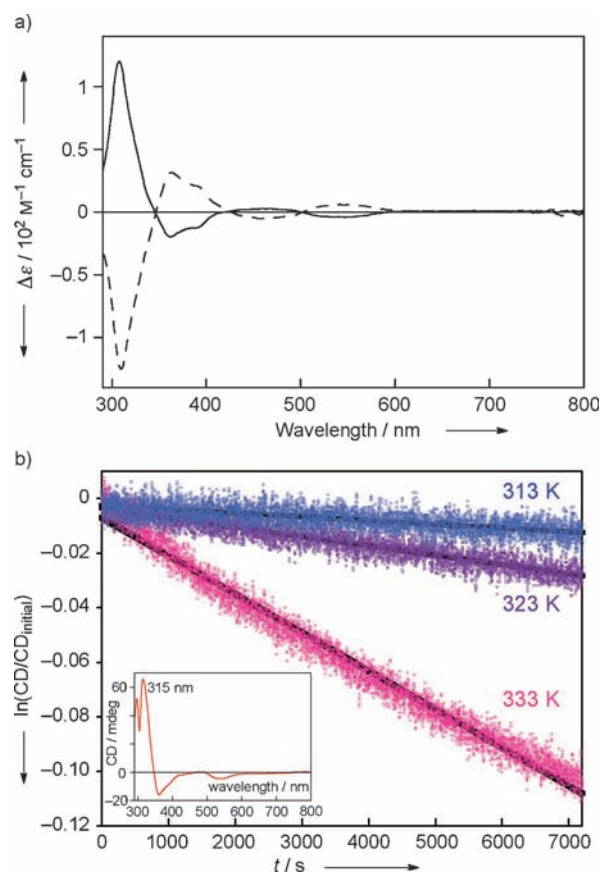


Figure 4. a) CD spectra of (*P*)-**1** (solid line, 1.0×10^{-4} M) and (*M*)-**1** (dashed line, 7×10^{-5} M) in toluene solution at 303 K under nitrogen atmosphere. b) Time-dependent decay profiles of the CD intensity of (*P*)-**1** (8×10^{-5} M) in *o*-xylene at 315 nm (see the inset CD spectrum) at 313 K (blue), 323 K (purple), and 333 K (pink). The solution was degassed and sealed under vacuum.

several thermodynamic parameters were determined from the Arrhenius plot and Eyring plot (see the Supporting Information). The activation energy $\Delta G^\ddagger$ at 303 K of **1** (111.7 kJ mol⁻¹) is slightly less than that of **6** (118.8 kJ mol⁻¹, see above) but significantly greater than that of [5]helicene (101.0 kJ mol⁻¹).^[23,27] Furthermore, it should be noted that the experimentally estimated half-life ($t_{1/2}$) for the racemization of chiral radicals **1** in *o*-xylene at 303 K is quite long ($t_{1/2} = 23$ days).^[28] All these experimental results clearly demonstrate that **1** is the first chiral neutral π -radical with high spin-delocalization and high configurational and chemical stability.

In summary, the first helicene-structured chiral phenalene neutral π -radicals have been designed, synthesized, and characterized. The high configurational and chemical stability of **1** plays a crucial role throughout the study, allowing us to examine the extensive spin-delocalization of the 3D π -electron network and the significant CD properties attributable to the helicenic chirality. Because of these unique features, the present system is intrinsically different from the previously reported chiral neutral radicals based on spin-localized nitroxide radicals bearing one or more asymmetric carbon centers.^[9,26] The solid-state magnetic and optical

properties of this kind of spin-delocalized chiral open-shell system are of great interest, and form the basis for the development of a new class of chiral molecular magnets^[10] and addressable matter electron-spin qubit (quantum bit) systems.^[29] The X-ray crystal structure analysis and magnetic susceptibility measurements of **1** are underway. Furthermore, we are currently investigating metal complexes of **1** as well as new helicene-structured chiral spin-delocalized air-stable neutral π -radicals based on hydrocarbon phenalenyl^[11,30] and oxophenalenoxyl^[11,12c,e] systems as new challenging materials in synthetic organic spin chemistry.^[11b]

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- [18] In the crystal, *rac*-**6** forms a one-dimensional structure through intermolecular N–H···N hydrogen bonds. For details, see the Supporting Information.
- [19] Under aerobic conditions most *rac*-**1** in solution at room temperature decomposed within a few days. TLC, ¹H NMR, and EI-MS analyses suggest that an air-oxidized phenalene derivative was formed as a main product.
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